## **Supplementary Information**

# Polymerization-pH Tailored RAFT-Mediated Polymerization-Induced Self-assembly for Ice Recrystallization Inhibiting Investigation

Huangbing Xu,<sup>a,b</sup> Teng Qiu,<sup>a,b,c</sup> Haotian Shi,<sup>a</sup> Xiaoqian Tian,<sup>b</sup> Xiaoyu Li,<sup>\*,a,b</sup> Longhai Guo<sup>\*,a,b,c</sup>

- a. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China.
- Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China.
- c. Beijing Engineering Research Center of Synthesis and Application of Waterborne Polymer, Beijing University of Chemical Technology, Beijing 100029, PR China

#### **Corresponding Authors**

- \*E-mail for Longhai Guo: guolh@mail.buct.edu.cn;
- \*E-mail for Xiaoyu Li: <u>lixy@mail.buct.edu.cn</u>

## **Table of Content**

1.	Synthesis of S,S'-bis (R,R'-dimethyl-R'-acetic acid)-trithiocarbonate (BDAAT).3
2.	The <sup>1</sup> H-NMR and the Conversion4
3.	The FTIR Spectra5
4.	The Characterization Results of PDMAA Macro-CTAs6
5.	The Characterization Results of PDMAA <sub>x</sub> -b-PDAAM <sub>y</sub> -b-PDMAA <sub>x</sub> Triblock8
6.	Characterizations of A <sub>28</sub> B <sub>y</sub> A <sub>28</sub> Triblock Copolymers13
7.	The Estimation on the Packing Parameter (P)14
8.	The Kinetic Studies of A <sub>28</sub> B <sub>400</sub> A <sub>28</sub> Copolymers16
9.	Other Influences on the Morphology of A <sub>28</sub> B <sub>y</sub> A <sub>28</sub> Copolymers18
10.	The IRI Activity of A <sub>28</sub> B <sub>y</sub> A <sub>28</sub> Triblock Copolymers20
11.	The DIS Results of A <sub>28</sub> B <sub>y</sub> A <sub>28</sub> Triblock Copolymers22
12.	The Single Ice Crystal Growth Assay of A <sub>28</sub> B <sub>y</sub> A <sub>28</sub> Triblock Copolymers23
13.	Reference24

#### 1. Synthesis of S,S'-bis (R,R'-dimethyl-R'-acetic acid)-trithiocarbonate (BDAAT)

Carbon disulfide (30.4 g, 0.4 mol), chloroform (119.4 g, 1.0 mol), acetone (58.1 g, 1.0 mol), and tetrabutylammonium hydrogen sulfate (2.68 g, 0.008 mol) were mixed with 133 mL n-hexane into a 2 L glass flask cooled with the ice-water mixture. 50 *wt*% Sodium hydroxide aqueous solution (224 g, 28 mol) was added dropwise into the flask over 90 min, the temperature was kept below 10 °C. Then 1000 mL water and 133 mL HCl were added to dissolve and acidify the mixture after 12 h reaction. The mixture was stirred for another 30 min with a nitrogen purge to remove excess acetone and filtered to get a yellow solid. The yellow solid was washed with water several times and dried in a vacuum oven. After that, further purification by recrystallization in acetone was carried out and the yellow crystalline solid was finally obtained. The benzyl-capped BDAAT was synthesized according to the reference.<sup>1</sup>

## 2. The <sup>1</sup>H-NMR and the Conversion



Figure S1. <sup>1</sup>H NMR spectra for BDAAT, PDMAA macro-CTA agent and PDMAA-b-PDAAM-b-PDMAA

copolymer.

$$\operatorname{conv}_{DMAA} = 1 - \frac{I_{6.75} + I_{6.08} + I_{5.64}}{3 \times DP_{th}} \times 100\%$$

$$(1)$$

$$\operatorname{conv}_{DMAA} = 1 - 3 \times (\frac{I_{6.21} + I_{6.02} + I_{5.51}}{I_{2.16}}) \times 100\%$$

#### 3. The FTIR Spectra



Figure S2. FTIR spectra of BDAAT, PDMAA macro-CTA agent and PDMAA-b-PDAAM-b-PDMAA

triblock copolymer.





Figure S3. (a) UV spectra of BDAAT with different concentrations  $(1.26 \times 10^{-5} \text{ mol/L} \sim 12.6 \times 10^{-5} \text{ mol/L})$  (b) and the calibration curve for concentration calculation.

by UV-vis using the peak at 308 nm for calibration. The calibration curve is provided in The mean DP for each macro-CTA was then determined in a methanol solution by the following equation:

$$DP = \frac{\frac{c_p}{c_{BDAAT}} - M_{BDAAT}}{M_m}$$
(3)

where  $c_p$  stands for the concentration of PDMAA in methanol solution,  $c_{BDAAT}$  stands for the concentration of the BDAAT in methanol solution, and  $M_{BDAAT}$  and  $M_m$  stand for the molecular weight of BDAAT and monomer DMAA, respectively.



**Figure S4.** (a) Elution profiles of GPC for the characterization of PDMAA<sub>2x</sub> (x = 18, 22, 25, 28, 35); (b) Elution profiles of GPC for the characterization of PDMAA<sub>19</sub>-*b*-PDAAM<sub>y</sub>-*b*-PDMAA<sub>19</sub> (y = 30, 60, 100, 140, 200, 300, 400, 500)

Entry	Molecular Structure	Target DP	Conv. <sup>a</sup> %	Exp. DP <sup>b</sup>	xc	$M_{n,theo}{}^d/10^3$	$M_{n,\;GPC}{}^e/\;10^3$	$M_w\!/M_n$
1	PDMAA <sub>38</sub>	30	> 99	38	19	3.3	3.8	1.14
2	PDMAA <sub>44</sub>	40	> 99	44	22	4.2	5.1	1.12
3	PDMAA <sub>50</sub>	50	> 99	50	25	5.2	5.4	1.18
4	PDMAA <sub>56</sub>	55	> 99	56	28	5.7	6.4	1.12
5	PDMAA <sub>70</sub>	60	> 99	70	35	6.2	8.9	1.19

Table S1. The characterization results of PDMAA macro-CTA with various DPs

<sup>a</sup> Monomer conversion calculated by <sup>1</sup>H NMR spectra

<sup>b</sup> Experimental DP calculated by UV spectra.

<sup>c</sup> x represents each block length of the asymmetrical PDMAA<sub>x</sub>-b-CTA-b- PDMAA<sub>x</sub>. x = DP/2.

<sup>d</sup> Theoretical  $M_n$  calculated by monomer conversion.

<sup>e</sup>  $M_{\rm n}$  measured by GPC.

## 5. The Characterization Results of PDMAA<sub>x</sub>-b-PDAAM<sub>y</sub>-b-PDMAA<sub>x</sub> Triblock

Table S2. Summary of the characterization data for all PDMAA<sub>x</sub>-PDAAM<sub>y</sub>-PDMAA<sub>x</sub> triblock

copolymers

Entry	2 <i>x</i>	2 <i>y</i>	pН	Conv. <sup>a</sup> /%	Z-average diameter/nm	PDI	M <sub>n, Theo</sub> <sup>b</sup> / 10 <sup>3</sup> g·mol <sup>-1</sup>	M <sub>n, GPC</sub> <sup>c</sup> / 10 <sup>3</sup> g·mol <sup>-1</sup>	Mw/ Mn	assigned morphology <sup>d</sup>
1		30		-	-	-	8.8	-	-	gel <sup>e</sup>
2		60	1	-	-	-	10.1	-	-	gel
3		100		-	-	-	16.9	-	-	gel
4	20	140	]	-	-	-	23.7	-	-	gel
5	38	200	2.5	-	-	-	33.8	-	-	gel
6		300		-	-	-	50.7	-	-	gel
7		400		-	-	-	67.6	-	-	gel
8		500		-	-	-	84.5	-	-	gel
9		30		-	-	-	8.8	-	-	gel
10		60	]	-	-	-	10.1	-	-	gel
11		100	]	-	-	-	16.9	-	-	gel
12	20	140	- 6	-	-	-	23.7	-	-	gel
13	38	200		-	-	-	33.8	-	-	gel
14		300		-	-	-	50.7	-	-	gel
15		400		-	-	-	67.6	-	-	gel
16		500		-	-	-	84.5	-	-	gel
17		30		100%	25	0.437	8.8	7.2	1.12	spheres
18		60		100%	37	0.259	10.1	10	1.30	spheres
19		100		100%	42	0.195	16.9	12.6	1.28	spheres+vesicles
20	20	140		100%	144	0.243	23.7	15.6	1.26	spheres+vesicles
21	38	200	) 8	100%	239	0.125	33.8	19.7	1.30	spheres+vesicles
22		300		100%	278	0.102	50.7	35.2	1.36	spheres+vesicles
23		400		100%	334	0.152	67.6	51.6	1.14	spheres
24		500		100%	338	0.071	84.5	66.8	1.42	spheres
25		40		-	-	-	11.1	-	-	gel
26		60		-	-	-	10.1	-	-	gel
27	1	80		-	-	-	13.5	-	-	gel
28	44	100	2.5	-	-	-	16.9	-	-	gel
29		120	]	-	-	-	20.3	-	-	gel
30		140	]	-	-	-	23.7	_	-	gel
31		160		-	-	-	27.0	-	-	gel

130         130         14         160         17         17         130         17         180           333         200         200         200         20         3.38         1.0         1.0         1.00           360         200         200         2.0         6.0         6.0         1.0         1.0         1.00         1.00           370         400         7.0         1.00				-				1	1	1	
33         1         200 (30)         200 (30)	32		180		-	-	-	30.4	-	-	gel
34         250         260           42.3	33		200		-	-	-	33.8	-	-	gel
36         300         40         -         50         50.7         -         0         1	34		250		-	-	-	42.3	-	-	gel
36     160     17     17     17     18     10     11     10     1     10       38     8     40     10     10     10.1     10.1     10.1     10       39     8     100     10     10.1     10.1     10.1     10     100       40     100     10     10.1     10.1     10.1     10     100       41     100     10     10.1     10.1     10.1     10     100       41     100     10     10.1     10.1     10.1     100     100       41     100     10     10.1     10.1     10.1     100     100       41     100     10     10.1     10.1     10.1     100     100       41     100     10     10.1     10.1     10.1     100     100       41     100     10.1     10.1     10.1     10.1     100     100       41     100     10.1     10.1     10.1     10.1     100     100       51     100     100     10.1     10.1     10.1     100     100       51     100     100     10.1     10.1     10.1     10.1     100 <t< td=""><td>35</td><td></td><td>300</td><td></td><td>-</td><td>-</td><td>-</td><td>50.7</td><td>-</td><td>-</td><td>gel</td></t<>	35		300		-	-	-	50.7	-	-	gel
37         9         40         0         0         1.1         0.1	36		400		-	-	-	67.6	-	-	gel
38         94         60         0         0.1	37		40		-	-	-	11.1	-	-	gel
39         40         100         1         1.3.5         1.0         1         Iggl           40         100         10         1.0	38		60	]	-	-	-	10.1	-	-	gel
40         100         100         100         100         100         100         100         100           41         100         120         -         -         20.3         -         -         0gd           43         140         100         100         -         23.7         -         0         0gd           43         100         100         -         30.4         -         0         0gd           44         100         100         -         30.4         -         0         0gd           46         200         -         -         30.4         -         0         0gd           47         300         -         -         60.7         -         0gd         0gd           48         -         -         -         -         -         07.0         0.1	39		80		-	-	-	13.5	-	-	gel
141         120         140         120         140         140           42         140         140         160         -         0         23.7         0         0         0gl           44         160         160         -         0         27.0         0.0         0         0gl           45         180         250         -         0         33.8         0         0         0gl           46         250         0         0.0         1.4         30.0         1.0         0.0         0.0           47         300         0         42.3         0.0         0         0.0         0.0           48         0         0         0.0         1.0         10.0         1.0         0.0         0.0           49         0         0         0.1         0.0         1.0         1.0         0.0         0.0         0.0         1.0         1.0         1.0         0.0         0.0         0.0         0.0         1.0         1.0         0.0         0.0         0.0         1.0         1.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0	40		100	]	-	-	-	16.9	-	-	gel
42         44         140         160         6         -         -         23.7         -         -         gel           44         160         160         -         -         27.0         -         -         gel           45         180         -         -         30.4         -         -         gel           45         200         -         -         43.38         -         -         gel           47         200         -         -         42.3         -         -         gel           48         -         0.0         -         42.3         -         -         gel           49         -         -         -         -         42.5         -         -         gel           40         -         -         -         -         50.7         -         -         gel           50         400         -         -         -         0.7         1.2         gel         -           51         90%         65         0.147         10.1         1.0         1.35         spheres+vesicles           53         100         100         152	41		120		-	-	-	20.3	-	-	gel
43         44         160         1         0         -         27.0         -         -         gel           44         180         200         -         -         30.4         -         -         gel           45         200         250         -         -         33.8         -         -         gel           46         300         -         -         60.7         -         -         gel           47         300         -         -         67.6         -         -         gel           49         -         -         -         67.6         -         -         gel           50         60         -         99%         56         0.147         10.1         10.7         1.32         spheres           50         55         60         120         99%         65         0.08         16.9         14.3         1.35         spheres+vesicles           55         100         100         105         0.069         27.0         18.8         1.19         spheres+vesicles           56         120         99%         152         0.069         27.0         18.2 <td< td=""><td>42</td><td></td><td>140</td><td></td><td>-</td><td>-</td><td>-</td><td>23.7</td><td>-</td><td>-</td><td>gel</td></td<>	42		140		-	-	-	23.7	-	-	gel
44         180         180         200         1         1         30.4         1         1         gel           46         200         250         1         1         33.8         1         1         gel           47         300         1         1         1         1         1         gel           48         400         1         -         1         50.7         -         1         gel           49         400         -         -         0         67.6         -         -         gel           50         60         9%         37         0.298         11.1         9.8         1.24         spheres           51         50         60         9%         46         0.152         13.5         11.5         1.27         spheres           52         100         100         105         20.3         15.1         1.4         spheres+vesicles           53         120         100%         107         0.05         23.7         16.2         1.25         spheres+vesicles           54         140         19         90%         150         0.06         33.8         20	43	44	160		-	-	-	27.0	-	-	gel
45         200	44		180		-	-	-	30.4	-	-	gel
46         250         250         1         -         42.3         -         -         gel           48         400         -         -         50.7         -         -         gel           49         400         -         -         67.6         -         -         gel           50         -         60         -         -         gel         -         gel           50         -         60         -         -         -         67.6         -         -         gel           51         -         60         -         -         0.00         1.11         9.8         1.24         spheres           53         -         60         99%         56         0.17         10.1         10.7         1.32         spheres+vesicles           54         100         99%         66         0.08         16.9         14.3         1.35         spheres+vesicles           55         100         100         0.05         2.37         16.2         1.2         spheres+vesicles           56         100         101         0.05         23.7         16.2         1.3         spheres+vesicles <td>45</td> <td></td> <td>200</td> <td>1</td> <td>-</td> <td>-</td> <td>-</td> <td>33.8</td> <td>-</td> <td>-</td> <td>gel</td>	45		200	1	-	-	-	33.8	-	-	gel
47         300         1         50.7           gel           48         400           67.6           gel           49           67.6           gel           50         5.0          60.         1.0         9.8         1.24         spheres           51         50         60         9.9%         5.6         0.147         10.1         10.7         1.32         spheres           51         80         95%         4.6         0.152         13.5         11.5         1.27         spheres           53         100         99%         6.6         0.08         16.9         14.3         1.35         spheres+vesicles           54         100         105         0.08         16.9         14.3         1.4         spheres+vesicles           55         100         107         0.05         23.7         16.2         1.25         spheres+vesicles           56         200         99%         175         0.115         30.4         19.3         1.35         spheres+vesicles           50         3	46		250		-	-	-	42.3	-	-	gel
4840067.6ggl49400370.29811.19.81.24spheres508099%560.14710.110.71.32spheres5199%560.14710.110.71.32spheres5399%650.0816.914.31.35spheres+vesicles54spheres+vesicles55spheres+vesicles56spheres+vesicles56spheres+vesicles56spheres+vesicles56spheres+vesicles5758 <td>47</td> <td></td> <td>300</td> <td>1</td> <td>-</td> <td>-</td> <td>-</td> <td>50.7</td> <td>-</td> <td>-</td> <td>gel</td>	47		300	1	-	-	-	50.7	-	-	gel
49404097%370.29811.19.81.24spheres506099%560.14710.110.71.32spheres5199%650.0811.51.151.27spheres5310093%650.0816.914.31.35spheres+vesicles5414016099%860.07320.315.11.4spheres+vesicles55160100%1070.0523.716.21.25spheres+vesicles5618099%1750.11530.419.31.34spheres+vesicles5720099%1920.05742.328.31.35spheres+vesicles5825030099%1920.05742.328.31.35spheres+vesicles5930096%2270.02650.737.21.42spheres6040094%2540.10267.659.81.36spheres6198%10013.5-2gel628010013.51.42spheres6310010013.5-3gel6410013.5gel6610010013.5gel6610010013.5<	48		400	1	-	-	-	67.6	-	-	gel
50         60         99%         56         0.147         10.1         10.7         1.32         spheres           51         95%         46         0.152         13.5         11.5         1.27         spheres           53         120         93%         65         0.08         16.9         14.3         1.35         spheres+vesicles           54         140         93%         65         0.08         16.9         14.3         1.35         spheres+vesicles           55         140         100%         107         0.05         23.7         16.2         1.25         spheres+vesicles           56         100%         152         0.069         27.0         18.8         1.19         spheres+vesicles           57         100%         152         0.069         27.0         18.8         1.19         spheres+vesicles           58         100%         152         0.069         27.0         18.8         1.19         spheres+vesicles           58         200         97%         186         0.064         33.8         20         1.32         spheres+vesicles           59         300         1227         0.026         50.7 <t< td=""><td>49</td><td></td><td>40</td><td></td><td>97%</td><td>37</td><td>0.298</td><td>11.1</td><td>9.8</td><td>1.24</td><td>spheres</td></t<>	49		40		97%	37	0.298	11.1	9.8	1.24	spheres
51 $80$ $95%$ $46$ $0.152$ $13.5$ $11.5$ $1.27$ spheres $53$ $100$ $93%$ $65$ $0.08$ $16.9$ $14.3$ $1.35$ spheres $spheres$ $54$ $140$ $120$ $99%$ $86$ $0.073$ $20.3$ $15.1$ $1.4$ $spheres+vecicles$ $55$ $1160$ $100%$ $107$ $0.05$ $23.7$ $16.2$ $1.25$ $spheres+vecicles$ $56$ $180$ $100%$ $152$ $0.069$ $27.0$ $18.8$ $1.19$ $spheres+vecicles$ $57$ $200$ $99%$ $175$ $0.115$ $30.4$ $19.3$ $1.34$ $spheres+vecicles$ $58$ $250$ $99%$ $192$ $0.057$ $42.3$ $28.3$ $1.35$ $spheres+vecicles$ $50$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ $spheres$ $60$ $140$ $-2.5$	50		60	1	99%	56	0.147	10.1	10.7	1.32	spheres
52 $100$ $93%$ $65$ $0.08$ $16.9$ $14.3$ $1.35$ spheres+vesicles $54$ $140$ $140$ $140$ $99%$ $86$ $0.073$ $20.3$ $15.1$ $1.4$ $spheres+vesicles$ $55$ $160$ $160$ $100%$ $107$ $0.05$ $23.7$ $16.2$ $1.25$ $spheres+vesicles$ $56$ $180$ $100%$ $152$ $0.069$ $27.0$ $18.8$ $1.19$ $spheres+vesicles$ $57$ $180$ $200$ $99%$ $175$ $0.115$ $30.4$ $19.3$ $1.34$ $spheres+vesicles$ $58$ $200$ $99%$ $192$ $0.057$ $42.3$ $28.3$ $1.35$ $spheres+vesicles$ $59$ $300$ $96%$ $227$ $0.026$ $50.7$ $37.2$ $1.42$ $spheres$ $60$ $400$ $51$ $-1$ $51.51$ $-1$ $21.62$ $51.61$ $-1$ $21.62$ $21.62$ <td>51</td> <td></td> <td>80</td> <td></td> <td>95%</td> <td>46</td> <td>0.152</td> <td>13.5</td> <td>11.5</td> <td>1.27</td> <td>spheres</td>	51		80		95%	46	0.152	13.5	11.5	1.27	spheres
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	52		100	1	93%	65	0.08	16.9	14.3	1.35	spheres+vesicles
54         44         140         8         100%         107         0.05         23.7         16.2         1.25         spheres+vesicles           56         180         160         100%         152         0.069         27.0         18.8         1.19         spheres+vesicles           57         200         99%         175         0.115         30.4         19.3         1.34         spheres+vesicles           58         250         99%         192         0.057         42.3         28.3         1.35         spheres+vesicles           59         300         96%         227         0.026         50.7         37.2         1.42         spheres           60         400         94%         254         0.102         67.6         59.8         1.36         spheres           61         400         94%         254         0.102         67.6         59.8         1.36         spheres           62         400         140 $-$ -         15.1         -         -         gel           63         100         1.4         94%         2.4         7.0         -         1.62         .         gel <tr< td=""><td>53</td><td></td><td>120</td><td></td><td>99%</td><td>86</td><td>0.073</td><td>20.3</td><td>15.1</td><td>1.4</td><td>spheres+vesicles</td></tr<>	53		120		99%	86	0.073	20.3	15.1	1.4	spheres+vesicles
55         144         160         8         100%         152         0.069         27.0         18.8         1.19         spheres+vesicles           56         180         99%         175         0.115         30.4         19.3         1.34         spheres+vesicles           57         200         97%         186         0.064         33.8         20         1.32         spheres+vesicles           58         250         99%         192         0.057         42.3         28.3         1.35         spheres           59         300         96%         227         0.026         50.7         37.2         1.42         spheres           60         400         94%         254         0.102         67.6         59.8         1.36         spheres           61         400         94%         254         0.102         67.6         59.8         1.36         spheres           62         80         -         -         15.1         -         -         gel           63         100         -         7         16.9         -         -         gel           64         160         180         -         -	54	4.4	140		100%	107	0.05	23.7	16.2	1.25	spheres+vesicles
56 $180$ $99%$ $175$ $0.115$ $30.4$ $19.3$ $1.34$ spheres+vesicles $58$ $200$ $250$ $97%$ $186$ $0.064$ $33.8$ $20$ $1.32$ spheres+vesicles $59$ $300$ $99%$ $192$ $0.057$ $42.3$ $28.3$ $1.35$ spheres+vesicles $60$ $400$ $96%$ $227$ $0.026$ $50.7$ $37.2$ $1.42$ spheres $60$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $60$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $60$ $160$ $  15.1$ $  gel$ $64$ $140$ $   16.9$ $  gel$ $66$ $140$ $    23.7$ <	55	44	160		100%	152	0.069	27.0	18.8	1.19	spheres+vesicles
57 $200$ $250$ $97%$ $186$ $0.064$ $33.8$ $20$ $1.32$ $spheres+vesicles$ $59$ $300$ $250$ $99%$ $192$ $0.057$ $42.3$ $28.3$ $1.35$ $spheres$ $60$ $400$ $96%$ $227$ $0.026$ $50.7$ $37.2$ $1.42$ $spheres$ $60$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ $spheres$ $61$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ $spheres$ $61$ $60$ $400$ $-1$ $-15.1$ $-1$ $-16$ $gel$ $64$ $100$ $-1$ $-1$ $16.9$ $-1$ $gel$ $64$ $140$ $1.40$ $-1$ $-1$ $23.7$ $-1$ $gel$ $66$ $180$ $2.5$ $-1$ $-1$ $33.4$ $-1$ $gel$ $66$ <t< td=""><td>56</td><td></td><td>180</td><td></td><td>99%</td><td>175</td><td>0.115</td><td>30.4</td><td>19.3</td><td>1.34</td><td>spheres+vesicles</td></t<>	56		180		99%	175	0.115	30.4	19.3	1.34	spheres+vesicles
58 $250$ $99%$ $192$ $0.057$ $42.3$ $28.3$ $1.35$ spheres $60$ $300$ $96%$ $227$ $0.026$ $50.7$ $37.2$ $1.42$ spheres $60$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $60$ $80$ $  15.1$ $  gel$ $63$ $100$ $   13.5$ $  gel$ $64$ $100$ $   16.9$ $  gel$ $64$ $140$ $   23.7$ $  gel$ $66$ $180$ $2.5$ $   30.4$ $  gel$	57		200	1	97%	186	0.064	33.8	20	1.32	spheres+vesicles
59 $300$ $96%$ $227$ $0.026$ $50.7$ $37.2$ $1.42$ spheres $60$ $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $66$ $67$ $60$ $50.7$ $59.8$ $1.36$ spheres $61$ $66$ $80$ $7$ $  15.1$ $  gel$ $63$ $60$ $7$ $  16.9$ $  gel$ $64$ $140$ $   16.9$ $  gel$ $66$ $140$ $   23.7$ $  gel$ $66$ $180$ $2.5$ $   30.4$ $  gel$ $67$ $250$ $   33.8$ $  gel$ $66$	58		250		99%	192	0.057	42.3	28.3	1.35	spheres
60 $400$ $94%$ $254$ $0.102$ $67.6$ $59.8$ $1.36$ spheres $61$ $60$ $60$ $60$ $60$ $  15.1$ $  gel$ $62$ $80$ $80$ $  13.5$ $  gel$ $63$ $100$ $   13.5$ $  gel$ $64$ $100$ $   16.9$ $  gel$ $64$ $140$ $   23.7$ $  gel$ $66$ $160$ $   23.7$ $  gel$ $67$ $160$ $   30.4$ $  gel$ $67$ $200$ $   33.8$ $  gel$ $68$ $300$ $    50.7$ $ -$ <td< td=""><td>59</td><td></td><td>300</td><td></td><td>96%</td><td>227</td><td>0.026</td><td>50.7</td><td>37.2</td><td>1.42</td><td>spheres</td></td<>	59		300		96%	227	0.026	50.7	37.2	1.42	spheres
	60		400	]	94%	254	0.102	67.6	59.8	1.36	spheres
	61		60		-	-	-	15.1	-	-	gel
	62		80	]	-	-	-	13.5	-	-	gel
	63		100		-	-	-	16.9	-	-	gel
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	64		140	1	-	-	-	23.7	-	-	gel
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	65	-	160	1	-	-	-	27.0	-	-	gel
67         200         -         -         33.8         -         -         gel           68         250         -         -         42.3         -         -         gel           69         300         -         -         50.7         -         -         gel           70         400         -         -         67.6         -         -         gel	66	50	180	2.5	-	-	-	30.4	-	-	gel
68         250         -         -         42.3         -         -         gel           69         300         -         -         -         50.7         -         -         gel           70         400         -         -         -         67.6         -         -         gel	67		200	1	-	-	-	33.8	-	-	gel
69         300         -         -         50.7         -         -         gel           70         400         -         -         -         67.6         -         -         gel	68	1	250	1	-	-	-	42.3	-	-	gel
70 400 67.6 gel	69		300	1	-	-	-	50.7	-	-	gel
	70	1	400	1	-	-	-	67.6	-	-	gel

71		500		-	-	-	84.5	-	-	gel
72		60		-	-	-	15.1	-	-	gel
73		80	1	_	-	-	13.5	-	-	gel
74		100			-	-	16.9	-	-	gel
75		140	1	-	-	-	23.7	-	-	gel
76		160	1		-	-	27.0	-	-	gel
77	50	180	6	_	-	-	30.4	-	-	gel
78		200	1	_	-	-	33.8	-	-	gel
79		250			-	-	42.3	-	-	gel
80		300	1	_	-	-	50.7	-	-	gel
81		400	1	_	-	-	67.6	-	-	gel
82		500	1	_	-	-	84.5	-	-	gel
83		60		96%	36	0.152	15.1	12.2	1.17	spheres
84		80	1	97%	63	0.092	13.5	13.7	1.19	spheres
85		100	1	98%	78	0.046	16.9	14.6	1.23	spheres
86		140	1	100%	168	0.117	23.7	16.8	1.28	spheres
87		160	1	99%	181	0.075	27.0	19.4	1.31	spheres
88	50	180	8	99%	184	0.053	30.4	19.7	1.22	spheres
89		200		100%	220	0.004	33.8	20.4	1.32	spheres
90		250	1	100%	193	0.045	42.3	30.6	1.33	spheres
91		300		99%	221	0.086	50.7	36.5	1.35	spheres
92		400	1	100%	259	0.044	67.6	60.7	1.43	spheres
93		500		99%	277	0.079	84.5	64.9	1.44	spheres
94		60		98%	33	0.146	15.7	11.2	1.20	spheres
95		80	1	99%	38	0.059	13.5	13.2	1.18	spheres
96		100		98%	56	0.019	16.9	14.9	1.39	spheres
97		120		99%	120	0.111	20.3	15.7	1.35	peanuts
98		140	1	100%	182	0.193	23.7	17.3	1.29	peanuts+worms
99		160		96%	316	0.358	27.0	19.5	1.37	peanuts+worms+vesicles
100		200		98%	607	0.222	33.8	24.2	1.25	tadpoles
101	57	250		99%	1398	0.245	42.3	33.7	1.38	tadpoles
102	56	300	2.5	99%	1139	0.217	50.7	40.0	1.25	tadpoles
103		350	1	98%	1718	0.262	59.2	55.6	1.40	tadpoles
104		400	]	97%	1237	0.191	67.6	61.7	1.40	vesicle string
105		450	]	99%	1692	0.235	76.1	67.5	1.38	vesicle string
106	1	500	]	100%	1955	0.292	84.5	71.1	1.42	vesicle string
107		550	]	100%	567	0.394	93.0	82.2	1.47	LCVs
108		600	]	100%	619	0.194	101.4	88.5	1.50	LCVs
109		700		100%	822	0.377	118.3	103.7	1.58	LCVs

110		800		100%	1025	0.142	135.2	115.4	1.57	LCVs
111		60		95%	46	0.151	15.7	11.1	1.26	spheres
112		80		98%	67	0.051	13.5	13.2	1.22	spheres
113		100		99%	101	0.049	16.9	14.6	1.37	spheres
114		120		97%	169	0.09	20.3	16.3	1.23	spheres
115		140		99%	198	0.091	23.7	17.7	1.38	spheres
116		160		100%	242	0.159	27.0	18.5	1.23	spheres+vesicles
117		200		96%	299	0.194	33.8	23.2	1.20	spheres+vesicles
118		250	1	98%	448	0.185	42.3	32.6	1.25	spheres+vesicles
119	56	300	6	99%	570	0.22	50.7	40.6	1.35	spheres+worms+vesicles
120		350		98%	1045	0.246	59.2	49.1	1.26	spheres+worms+vesicles
121		400		97%	837	0.569	67.6	54.9	1.34	spheres+vesicles
122		450		100%	525	0.141	76.1	59.0	1.40	LCVs
123		500		100%	619	0.24	84.5	69.3	1.39	LCVs
124		550		99%	638	0.118	93.0	72.0	1.46	LCVs
125		600		100%	663	0.287	101.4	81.3	1.54	LCVs
126		700	1	100%	690	0.31	118.3	101.7	1.55	LCVs
127		800	1	100%	756	0.277	135.2	114.6	1.57	LCVs
128		60		99%	39	0.242	15.7	12.3	1.29	spheres
129		80	1	99%	56	0.104	13.5	14.3	1.22	spheres
130		100		98%	74	0.089	16.9	14.9	1.29	spheres
131		120		100%	97	0.033	20.3	15.2	1.25	spheres
132		140		98%	115	0.024	23.7	16.8	1.37	spheres
133		160		100%	126	0.028	27.0	18.3	1.23	spheres
134		180		100%	164	0.066	30.4	23.9	1.33	spheres
135	56	200	8	100%	144	0.058	33.8	25.7	1.27	spheres
136		250		100%	177	0.05	42.3	30.4	1.38	spheres
137		300		100%	183	0.048	50.7	42.5	1.37	spheres
138		400		100%	202	0.042	67.6	46.4	1.34	spheres
139		500		99%	218	0.102	84.5	73.2	1.49	spheres
140		600		100%	234	0.107	101.4	80.5	1.54	spheres
141		700		100%	240	0.077	118.3	104.5	1.47	spheres
142		800		100%	245	0.17	135.2	117.6	1.51	spheres
143		100		100%	92	0.058	23.8	14.6	1.24	spheres
144	70	250	25	100%	155	0.241	42.3	34.6	1.21	spheres
145	/0	400	2.3	100%	116	0.231	67.6	48.9	1.33	spheres
146		500		100%	105	0.226	84.5	72.4	1.24	spheres
147	70	100	6	99%	58	0.121	23.8	15.3	1.38	spheres
148		250		100%	118	0.027	42.3	35.5	1.38	spheres

149		400		100%	178	0.034	67.6	46.3	1.26	spheres
150		500		100%	170	0.064	84.5	73.6	1.40	spheres
151		100		98%	73	0.097	23.8	14.4	1.35	spheres
152	70	250	0	97%	113	0.033	42.3	32.7	1.37	spheres
153	/0	400	0	100%	188	0.045	67.6	49.0	1.31	spheres
154		500	]	100%	208	0.046	84.5	75.8	1.31	spheres

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy;

<sup>b</sup> determined by DLS on 0.5 wt% dispersions diluted by 0.05M NaCl aqueous solution;

<sup>c</sup>  $M_{n,theo} = DP_{PDMAA} \cdot M_{DMAA} + DP_{PDAAM} \cdot M_{DAAM};$ 

<sup>d</sup> determined by TEM on 0.5 wt% dispersions diluted by 0.05M NaCl aqueous solution;

<sup>e</sup> gelation occurred as  $DP_{PDMAA} = 38$ , 44, 50 when the polymerization was performed under the pH= 2.5 or 6 at the midway of the PISA. All the PISA were conducted using a magnetic stirring at the bottom, gelation would occur from the top to the bottom of the dispersion and finally to a free-standing physical soft gel as the polymerization processed, which would lead to inaccuracy of the conversion and GPC and the morphology so the results were not recorded in this table.

## 6. Characterizations of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> Triblock Copolymers



Figure S5. Zeta-potential for A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> PISA particles prepared at different polymerization pH.



**Figure S6.** TEM images for  $A_{28}B_yA_{28}$  PISA particles prepared at the polymerization pH = 6 (a-l), and 8 (m-p).





Figure S7. The evolution of packing parameter (*P*) as the function of *y* for PISA particles of  $A_{28}B_yA_{28}$ prepared at different polymerization pH.

The basic data was from the TEM images. The packing parameter (P) is defined as :

$$P = \frac{v}{a_0 l_0} \tag{5}$$

where *v* is the volume of the hydrophobic segment,  $l_0$  is the length of the hydrophobic segment, and  $a_0$  is the effective area of the hydrophilic headgroups.<sup>2</sup>

The volume of the hydrophobic block *v* could be estimated through:

$$v = v_{DAAM} y \tag{6}$$

where  $v_{DAAM}$  is the volume of the DAAM monomer and y is the polymerization degree of the DAAM block.

 $l_0$  is estimated by the radius (half of the average diameter, *D*) of the spheres and cylinders or the wall thickness of the vesicles. Therefore, the packing parameter could be calculated through:

$$P = \frac{2v_{DAAM}y}{a_0 D} \tag{7}$$

Assuming 1/3 as the critic value of *P*. At that point, spherical assemblies would be obtained. However, the morphology transition would happen as soon as the value of *P* exceeds 1/3. For example, for polymerization pH = 2.5, the  $A_{28}B_{100}A_{28}$  could be chosen through the TEM images as at a transition critical point (*P* = 1/3), and *a*<sub>0</sub> can be calculated according to equation (7) by

$$\frac{1}{3} = \frac{2 * v_{DAAM} * 100}{a_0 * 63} \tag{8}$$

which gives  $a_0 = 9.53v_{DAAM}$ . Then the packing parameter of  $A_{28}B_yA_{28}$  PISA particles under polymerization pH = 2.5 can be calculated. The packing parameters of  $A_{28}B_yA_{28}$ nanoparticles under polymerization pH = 6 and 8 are calculated through the same method using  $A_{28}B_{140}A_{28}$  and  $A_{28}B_{600}A_{28}$  as the critical point, respectively. The diameter (*D*) of the particles (diameter of spheres and cylinders or the wall thickness of the vesicles) was the statistical results by the average of the diameters of ten particles in the TEM images for each sample via the software *Image J*.



## 8. The Kinetic Studies of A<sub>28</sub>B<sub>400</sub>A<sub>28</sub> Copolymers

**Figure S8.** Plots of  $D_z$  (blue dots) and DAAM monomer conversion (red squares) as the function of time for  $A_{28}B_{400}A_{28}$  polymerized at pH = (a) 2.5, (b) 6, (c) 8; evolution of  $M_n$  (blue circles) and dispersity  $(M_w/M_n, \text{ red dots}) vs.$  DAAM conversion for the RAFT-PISA of  $A_{28}B_{400}A_{28}$  polymerized at pH = (d) 2.5, (e) 6, (f) 8.



**Figure S9.** Plots of  $D_z$  (blue dots) and DAAM monomer conversion(red squares) as the function of time for benzyl-capped A<sub>28</sub>B<sub>400</sub>A<sub>28</sub> PISA particles prepared at the polymerization pH = (a) 2.5 and (b) 8; (c) TEM images of A<sub>28</sub>B<sub>400</sub>A<sub>28</sub> PISA particles at different reaction time/kinetic conversions under different polymerization pH are presented in.

## 9. Other Influences on the Morphology of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> Copolymers



Figure S10.  $D_z$  of PISA particles of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> as-prepared at the polymerization pH = 2.5 and that post-





Figure S11.  $D_z$  and TEM morphology of  $A_{28}B_yA_{28}$  PISA particles prepared at the polymerization pH =

2.5 for four freeze-thaw cycles.



Figure S12. TEM images for  $A_{28}B_yA_{28}$  PISA particles polymerized under different NaCl concentrations.

## 10. The IRI Activity of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> Triblock Copolymers



Figure S13. Optical microscope images of recrystallized ice crystals of 0.05 M NaCl at different pHs.



Figure S14. Optical microscope images of recrystallized ice crystals with the participation of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub>

PISA particles with different normalized concentrations of [PDMAA].



Figure S15. MLGS of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> PISA particles as the function of (a) [PDMAA] and (b)solid content.



**Figure S16.** MLGS and fractal dimension (*D*) as the function of *y* for  $A_{28}B_yA_{28}$  PISA particles prepared

at the polymerization pH = (a) 2.5 and (b) 6.

## 11. The DIS Results of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> Triblock Copolymers



Figure S17. Sucrose-assisted dynamic ice shaping for (a)  $A_{28}B_{100}A_{28}$  (pH = 2, spheres,  $D_z = 56$  nm) (b)

 $A_{28}B_{300}A_{28}$  (pH = 2, tadpoles,  $D_z = 1139$  nm) (c)  $A_{28}B_{400}A_{28}$  (pH = 2, vesicle strings,  $D_z = 1237$  nm) (d)

 $A_{28}B_{600}A_{28}$  (pH = 2, LCVs,  $D_z = 619$  nm) (e)  $A_{28}B_{200}A_{28}$  (pH = 6, spheres + vesicles,  $D_z = 299$  nm) (f)

 $A_{28}B_{300}A_{28}$  (pH = 6, spheres + vesicles + worms,  $D_z = 570$  nm) (g) 30% sucrose aqueous solution The

scale bar is 100 µm.



#### 12. The Single Ice Crystal Growth Assay of A<sub>28</sub>B<sub>y</sub>A<sub>28</sub> Triblock Copolymers

Figure S18. Growth processes of single ice crystals in 1 mg/mL dispersion of (a)  $A_{28}B_{100}A_{28}$  (pH = 2, spheres,  $D_z = 56$  nm), (b)  $A_{28}B_{300}A_{28}$  (pH = 2, tadpoles,  $D_z = 1139$  nm), (c)  $A_{28}B_{400}A_{28}$  (pH = 2, vesicle strings,  $D_z = 1237$  nm), (d)  $A_{28}B_{600}A_{28}$  (pH = 2, LCVs,  $D_z = 619$  nm), (e)  $A_{28}B_{200}A_{28}$  (pH = 6, spheres + vesicles,  $D_z = 299$  nm) and (f)  $A_{28}B_{300}A_{28}$  (pH = 6, spheres + vesicles + worms,  $D_z = 570$  nm). The scale bar is 50 µm.

## 13. Reference

- 1. M. Chen, S. Deng, Y. Gu, J. Lin, M. J. MacLeod and J. A. Johnson, *J Am Chem Soc*, 2017, **139**, 2257-2266.
- 2. J. N. Israelachvili, *Intermolecular and surface forces*, ACADEMIC PR, 1992.